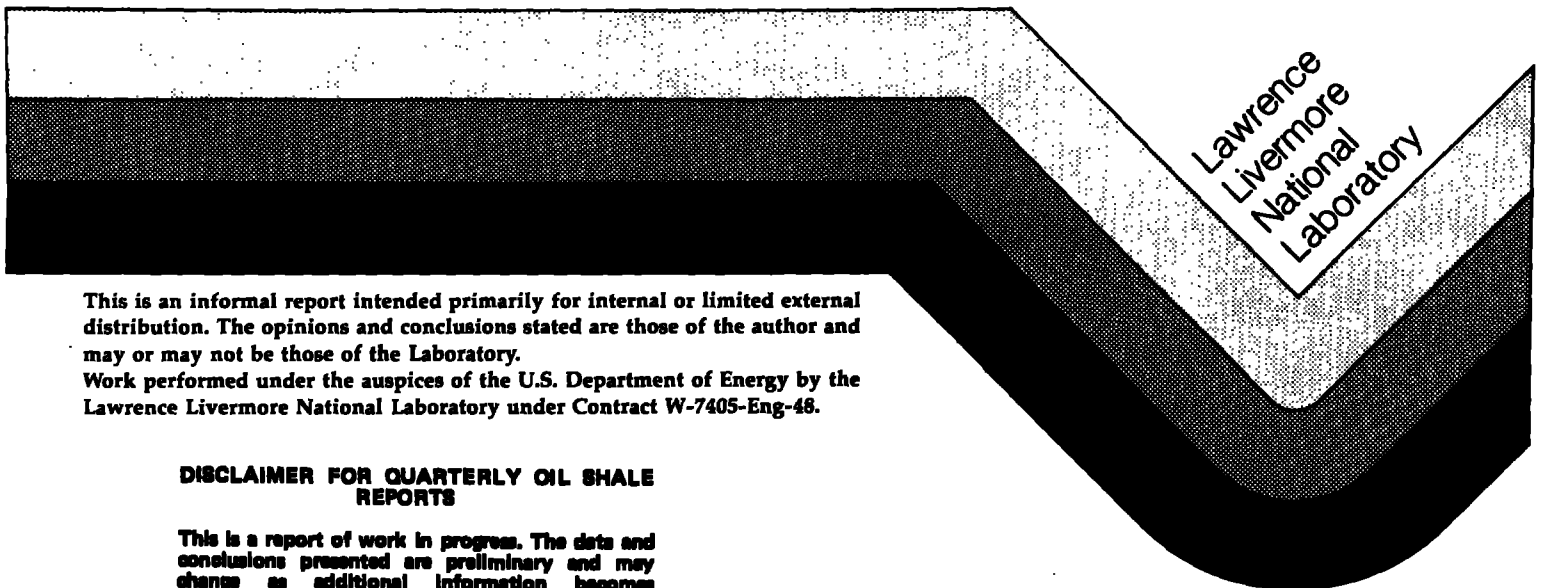CIRCULATION COPY
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LAWRENCE LIVERMORE NATIONAL LABORATORY
OIL SHALE PROJECT QUARTERLY REPORT

JULY - SEPTEMBER 1984

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For
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I. RETORT MODELING

Additional parameter studies using our moving-bed retort model were completed for an external-combustion, hot gas retort. Previously reported studies focused on effects of variations in the temperature and flow rate of the recycle gas and the dimensions of the retort. More recently, we investigated the effects of variations in shale grade, water content, flow rate, particle size, and bed porosity. We also considered effects of permeability contrast within a retort.

A high water content (free or bound water) in the shale has very detrimental effects on the operation of the retort, causing marked increases in compressor power requirements as well as in the heat loads at both the recycle heater and the product condenser. The effects of grade variations are much less pronounced, being predominantly beneficial for higher grades. Our model calculations, however, do not account for attrition of the shale particles. For the higher grade (150 L/Mg or 36 gal/ton), attrition may produce enough fine material to preclude satisfactory operation of the retort. Variations in shale flow rate, particle size, and bed porosity cause significant effects in the pressure drop and, hence, in the compressor power requirements. The oil yield, however, is nearly independent of these variations, as long as a high enough flow rate of recycle gas is used to give nearly complete pyrolysis of the outlet shale.

In all cases discussed so far it is presumed that the permeability of the bed is constant and the gas flow is uniform. Experience with packed-beds of oil shale demonstrates that uniform permeability is very difficult if not impossible to obtain. Variations in permeability can therefore be expected and will seriously degrade the performance of hot gas retorts. While permeability contrasts cannot be directly investigated with a one-dimensional

model, we used the model to gain some insight into the magnitude of the effects. As an example, let us consider a retort in which half of the cross-sectional area and volume are replaced with shale having a bed porosity of 56% (approximately 50% increase in gas flow rate) as compared to the base case of 45%. A model calculation for 56% porosity was combined with the base case calculation to estimate some of the operating characteristics of a composite retort with two different permeability regions. We used the same linear shale velocity as in the base case (3.43 m/hr at the top cross section of the retort) and the same pressure drop across the retort.

The full gas flow must be maintained in the region of lower permeability or the retorting will be incomplete. The presence of heavy oil or partially retorted kerogen in partially retorted shale will very likely make the shale cohesive and may obstruct the flow of shale through the retort.

In order to maintain sufficient gas flow in the region of low permeability it is necessary to increase the volume flow of gas by 39% for the entire composite retort compared to the base case. This greater gas flow increases the gas exit temperature to 182°C for the composite retort as compared to 68°C for the base case. This gas will now contain more than a third of the product oil as vapor and, if circulated through the retort as we proposed for the base case, will increase cracking from a negligible amount in the base case to nearly 2% F.A. The exact amount is uncertain because we have considered only the fraction of oil above its boiling point, used the rates measured for the highest boiling fraction being recycled and assumed a residence time of 10 s at 525°C.

This cracking loss and the lower mass rate of processing in the low porosity region combine to require a 10% increase in retorting units for a 50,000 barrel/day plant. Cracking may be reduced by cooling the recycle gas

and removing the product vapor from the gas stream. As in previous cases, we
did not cool the offgas prior to recycling it. If the offgas must be cooled
to avoid cracking losses or, more likely, to avoid deposition of solid in the
gas heater, then the heat load at both the offgas condenser and the recycle
heater will be greatly increased. Our base case, then, gives an overly
optimistic picture of the retort operation. The composite case closely
represents an actual retort with nonuniform gas flow assuming that gas can be
pumped directly through the gas heater without cooling to remove oil and
prevent solids deposition in the heater.

In summary, the LLNL one-dimensional model for simulating oil shale
retorting in an aboveground, moving-bed retort was applied to the indirect
mode of operation in which externally heated recycle gas provides the heat
required for the retorting process. Variations in recycle-gas temperature and
flow rate, shale flow rate, shale grade, water content, particle size
distribution, bed porosity, uniformity of porosity, and retort dimensions were
studied.

A high recycle-gas temperature minimizes the required recycle-gas flow
rate and, therefore, has the desirable effects of decreasing the retort
pressure drop and the compressor power. The temperature, however, must be
kept below approximately 525°C in order to avoid appreciable cracking of the
light-oil fraction which may be present in the recycle gas. Below this
temperature the cracking of newly-generated oil within the retort will also be
insignificant.

High retort pressure drop may be a key problem for hot-gas retorting. In
this parameter study the pressure drop ranged from 0.06 to 1.10 atm, depending
on the operating conditions. The resulting compressor power required for cir-
culation of the recycle gas in these two extreme cases ranged from 5 to 144 MW.

The pressure drop is particularly sensitive to the shale processing rate per unit reactor, shale particle size, and water content. The modeling results also illustrate how the size and shape of the retort affect the pressure drop.

The degree of pyrolysis of the outlet shale is a sensitive function of recycle-gas flux. Thus, operational problems may be present unless a high enough gas flux is used to ensure that flow nonuniformities do not cause localized regions of shale agglomeration due to incomplete pyrolysis of the kerogen or incomplete vaporization of the heavy oil components that are unable to flow out of the pyrolysis zone. Even more careful attention to start-up procedures may be required to avoid cohesion resulting from incomplete retorting.

The use of excess gas will almost certainly be necessary to compensate for nonuniform flow of gas through the retort. The resulting increase in exit gas temperature will require additional cooling capacity. These effects will combine to require more or larger retorts, more compressors, and more heat exchange capacity than would be expected if the flow were uniform.

II. SULFUR CONTAINING GASES BY TRIPLE QUADRUPOLE MASS SPECTROMETER (TQMS), BOTH GRAB AND ON-LINE ANALYSIS.

We have been evaluating the results for hydrogen sulfide and trace sulfur containing gases taken from the pyrolysis portion of the retort after leaving the oil condensers, as determined by the triple quadrupole mass spectometer (TQMS) for the retort runs R-2 through R-7. These runs were conducted in our hot solid retort system consisting of a fluidized bed pyrolyzer, a cascading bed combustor, and recirculating gas and solid streams. Differences had been

noted between determinations of the H_2S by Draeger tubes and the portable

on-line mini-quadrupole mass spectrometer (Analog Technology Corp. Automated

Trace Gas Monitor Model 2001), and the grab samples run on the TQMS.

Therefore, the TQMS was moved next to the retort for on-line analysis so that

direct comparisons could be made between the TQMS and the portable quad MS.

When these comparisons were made for retort R-7, no significant differences

were found between the three methods for determining H_2S. This indicated

that there was indeed a problem with the grab sample determinations for R-2

through R-6.

Initially, we assumed that the major problem was adsorption in the sample

bottles themselves, even though analyses were performed less than an hour

after samples were taken. This was probably the case for the very low results

found from R-2 because the sample bottles were new and had not been properly

conditioned. Great care was taken to pretreat the sample bottles with H_2S

after this run, and although the results were higher, they were still low when

compared with the on-line mini-quad MS.

For on-line analysis, the TQMS was interfaced to a sophisticated mass

spectrometer inlet system borrowed from the Underground Coal Gasification

Project. This inlet was used to properly adjust the sample pressure from the

flowing gas stream coming from the retort. This inlet also contained

standardization and grab sample manifolds, so a grab sample was taken on

retort R-7 and analyzed using the grab sample manifold. The grab sample was

also analyzed in the same way as grab samples from R-2 through R-6. To our

surprise, the grab sample gave results very comparable to the on-line results

when the gas inlet system was used, whereas low results were obtained with the

procedure we had used previously as described in detail in Appendix A.

Because the low values for grab samples could not be blamed entirely on absorption in the containers, this forced us to review our sample introduction procedures. Through a series of carefully controlled experiments (see Appendix A), we were able to show that the results for H_2S and trace sulfur containing gases were low by an amount that could be determined based on the gross composition of the gas. The error was due to a complex mix of ion gauge response, gas viscosities and pumping speeds.

We have corrected all data from the grab samples, and the tabulations in Table 1 show the corrected data. It can be seen in data from R-5 and R-6 where Draeger tube and on-line MS data is included, that the TQMS data is now very comparable to the other methods for H_2S.

We have also carried out an extensive set of experiments to verify the results from the on-line TQMS for R-7. In particular, dilution experiments were done with our 200 ppm standards. We have been able to show that the instrument and the sophisticated inlet system are linear from a few ppm to 200 ppm for trace sulfur species and from a few ppm to 1000 ppm for H_2S. We nave also been able to verify the accuracy of our H_2S determinations, using three different known standards.

Figures 1 through 6 show H_2S and various trace sulfur containing gases as determined by the TQMS on-line for retort R-7. The pulse in intensity near the end of the run seen in Figures 1, 2, and 3 is due to an approximately one minute stop of the star valve feeding combusted shale to the pyrolysis region. The shape of the thiophene and methylthiophene curves are proportional to the exit gas temperature from the condensers (which was proportional to air temperature), and shows that these species partially condense in the oil.

Table 1. Sulfur containing gases in ppm as determined by triple
quadrupole mass spectrometry using grab samples. All tables
are corrected values - corrected to coal gas inlet
conditions.

R-2

| Date of Retort | | 28-Mar-84 | | |
Time Into Experiment	:01	:14	:34	:43
Hydrogen sulfide	4.	1.	3.	1.
Methanethiol	7.	3.	1.	1.
Ethanethiol	6.	1.	< 1.	< 1.
Propanethiol	1.	< 1.	< 1.	< 1.
Dimethyl sulfide	< 4.	< 4.	< 4.	< 4.
Dimethyl disulfide	13.	3.	1.5	0.3
Carbonyl sulfide	6.	3.	< 1.	< 1.
Carbon disulfide	< 1.	< 1.	< 1.	< 1.
Thiophene	40.	26.	8.4	9.
Methyl thiophene	63.	45.	15.	15.

Note: The sample containers used for these grab samples had not been
pretreated with H_2S containing gases. In addition, the containers for the
.34 and .43 minute samples contained brass valves which are more reactive to
H_2S than stainless steel.

R-3

Date of Retort			4-Apr-84		
Time Into Experiment	:02*	:03	:15	:31	:35
Hydrogen sulfide	62.	46.	75.	95.	72.
Methanethiol	9.	9.	12.	12.	11.
Ethanethiol	4.	4.	4.	4.	5.
Propanethiol	1.	3.	1.	1.	2.
Dimethyl sulfide	< 4.	< 4.	< 4.	< 4.	< 4.
Dimethyl disulfide	0.1	0.4	0.4	0.4	0.3
Carbonyl sulfide	5.	5.	4.	4.	5.
Carbon disulfide	< 1.	< 1.	< 1.	< 1.	< 1.
Thiophene	9.9	18.	22.	21.	24.
Methyl thiophene	6.9	32.	38.	35.	38.

* Sample in Mylar bag, all others in stainless steel bottles.

R-4

Date of Retort			3-May-84		
Sample Number	1*	3	8	16	22
Hydrogen sulfide	115.	75.	99.	118.	138.
Methanethiol	8.	6.	7.	9.	7.
Ethanethiol	3.	2.	3.	2.	2.
Propanethiol	2.	2.	2.	2.	< 1.
Dimethyl sulfide	< 4.	< 4.	< 4.	< 4.	< 4.
Dimethyl disulfide	1.4	0.5	0.3	0.3	0.4
Carbonyl sulfide	5.	5.	5.	5.	7.
Carbon disulfide	< 1.	< 1.	< 1.	< 1.	< 1.
Thiophene	29.	29.	28.	30.	32.
Methyl thiophene	41.	41.	45.	40.	47.

* Note: The retort had not reached steady-state when this sample was taken.

R-5

Date of Retort		15-May-84	
Sample Number	5	11	13*
Time	11:52	12:20	12:30
H_2S by Draeger tube	40.	100.	---
H_2S by on-line MS	77.	110.	---
Hydrogen sulfide	84.	116.	78.
Methanethiol	14.	11.	11.
Ethanethiol	5.	3.	2.
Propanethiol	3.	2.	2.
Dimethyl sulfide	< 4.	< 4.	< 4.
Dimethyl disulfide	5.	0.7	0.7
Carbonyl sulfide	5.	5.	5.
Carbon disulfide	< 1.	< 1.	< 1.
Thiophene	28.	24.	26.
Methyl thiophene	42.	36.	37.

* Note: Sample 13 was the only sample taken as a flow-through. Sample 13 was
taken after flow in the retort was reduced due to a plugged filter.
Reduced H_2S in this low flow sample is probably due to reaction with
the iron pipe since gas has longer residence time in the system.

R-6

Date of Retort			24-May-84			
Sample number	1	8	19	40	45	46*
Time Into Experiment	11:07	11:35	12:30	14:30	14:59	15:04
H_2S by Draeger tube	60.	90.	67.	60.	90.	---
H_2S by on-line MS	104.	110.	107.	105.	108.	104.
Hydrogen sulfide	90.	95.	73.	107.	77.	77.
Methanethiol	11.	8.	6.	8.	6.	6.
Ethanethiol	6.	5.	3.	3.	3.	3.
Propanethiol	7.	3.	2.	6.	2.	2.
Dimethyl sulfide	< 4.	< 4.	< 4.	< 4.	< 4.	< 4.
Dimethyl disulfide	5.	1.	0.9	.3	.6	.8
Carbonyl sulfide	4.	3.	3.	5.	3.	3.
Carbon disulfide	< 1.	< 1.	< 1.	< 1.	< 1.	< 1.
Thiophene	22.	21.	23.	32.	27.	28.
Methyl thiophene	37.	30.	37.	43.	44.	46.

*Note: Sample #46 was a flow through sample.

Figure 1

Figures are corrected data.

H2S DETERMINED BY THE TQMS FOR R-7

H2S DETERMINED BY THE MINI-QUAD MS FOR R-7

Figure 2

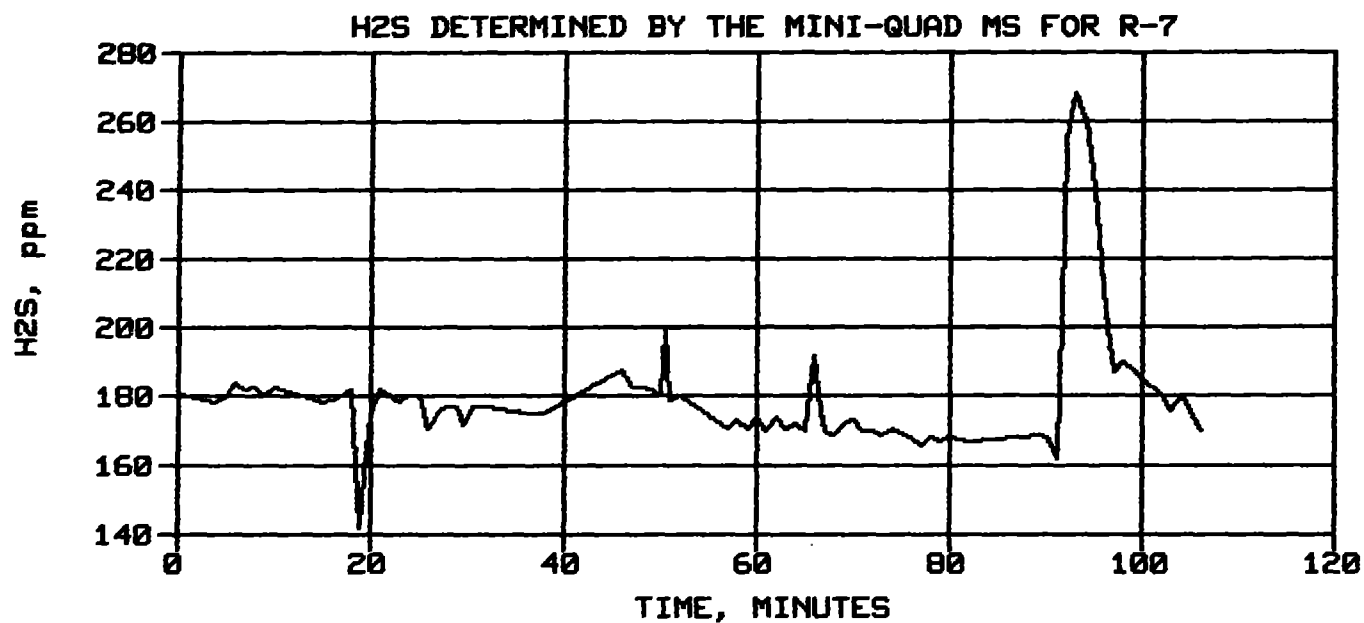
OIL SHALE STEADY-STATE RETORT R-7, START TIME 10:52 AM (TQMS)
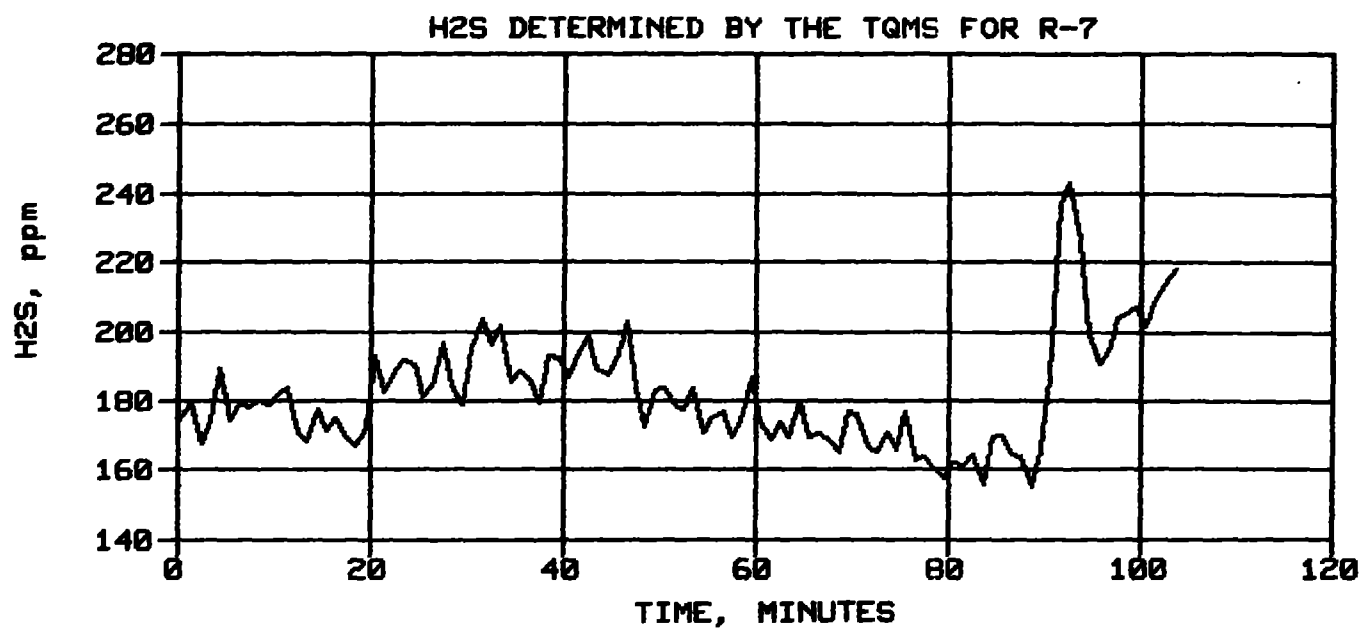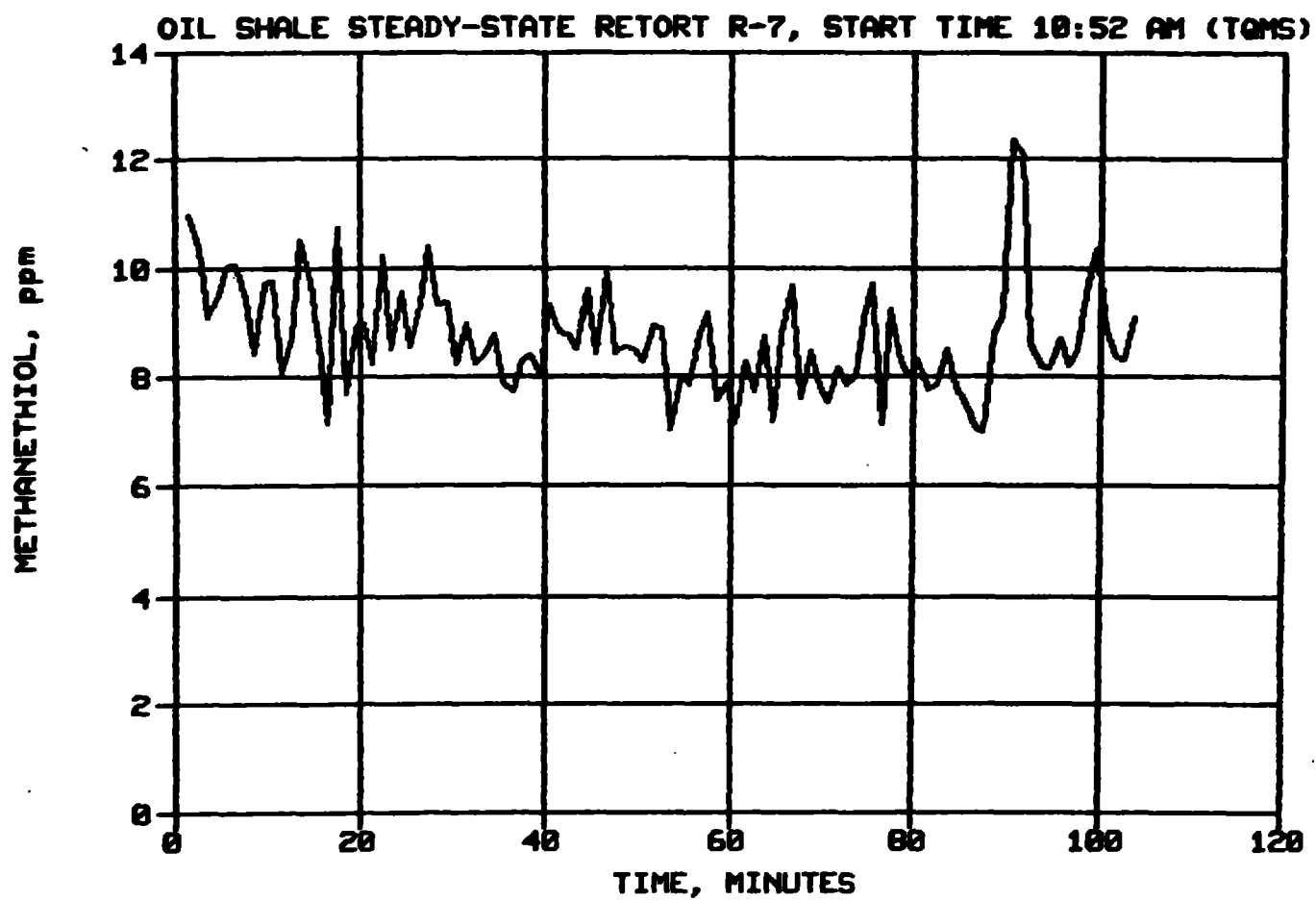
Figure 3

OIL SHALE PROCESS GAS STEADY-STATE RETORT R-7, START TIME 10:52 AM (TQMS)

Figure 4
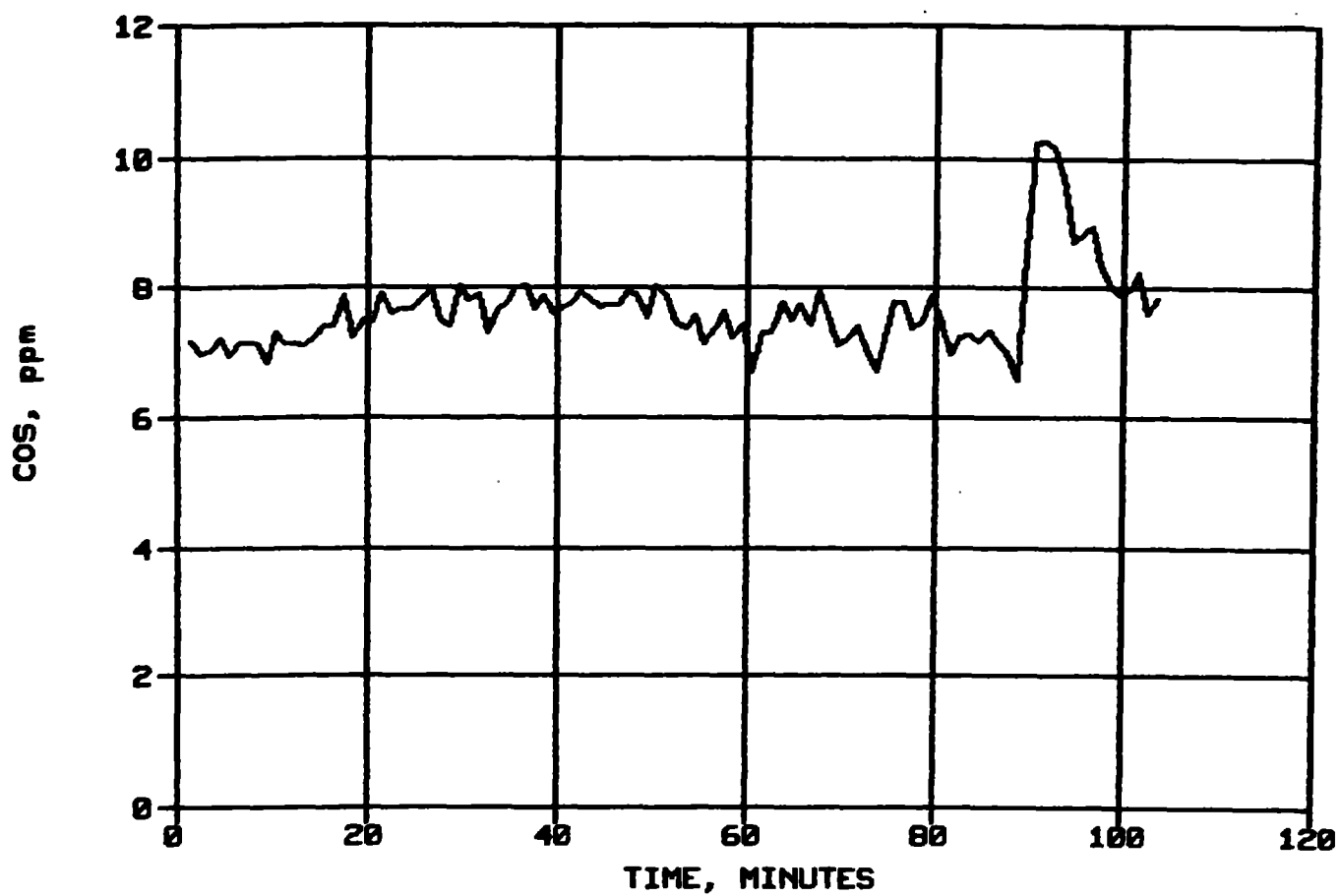
OIL SHALE STEADY-STATE RETORT R-7, START TIME 10:52 AM (TOMS)

Figure 5

OIL SHALE STEADY-STATE RETORT R-7, START TIME 10:52 AM (TOMS)

Figure 6

GAS TEMPERATURE LEAVING FINAL CONDENSER, RETORT R-7

OIL SHALE STEADY-STATE RETORT R-7, START TIME 10:52 AM (TQMS)

OIL SHALE STEADY-STATE RETORT R-7, START TIME 10:52 AM (TQMS)
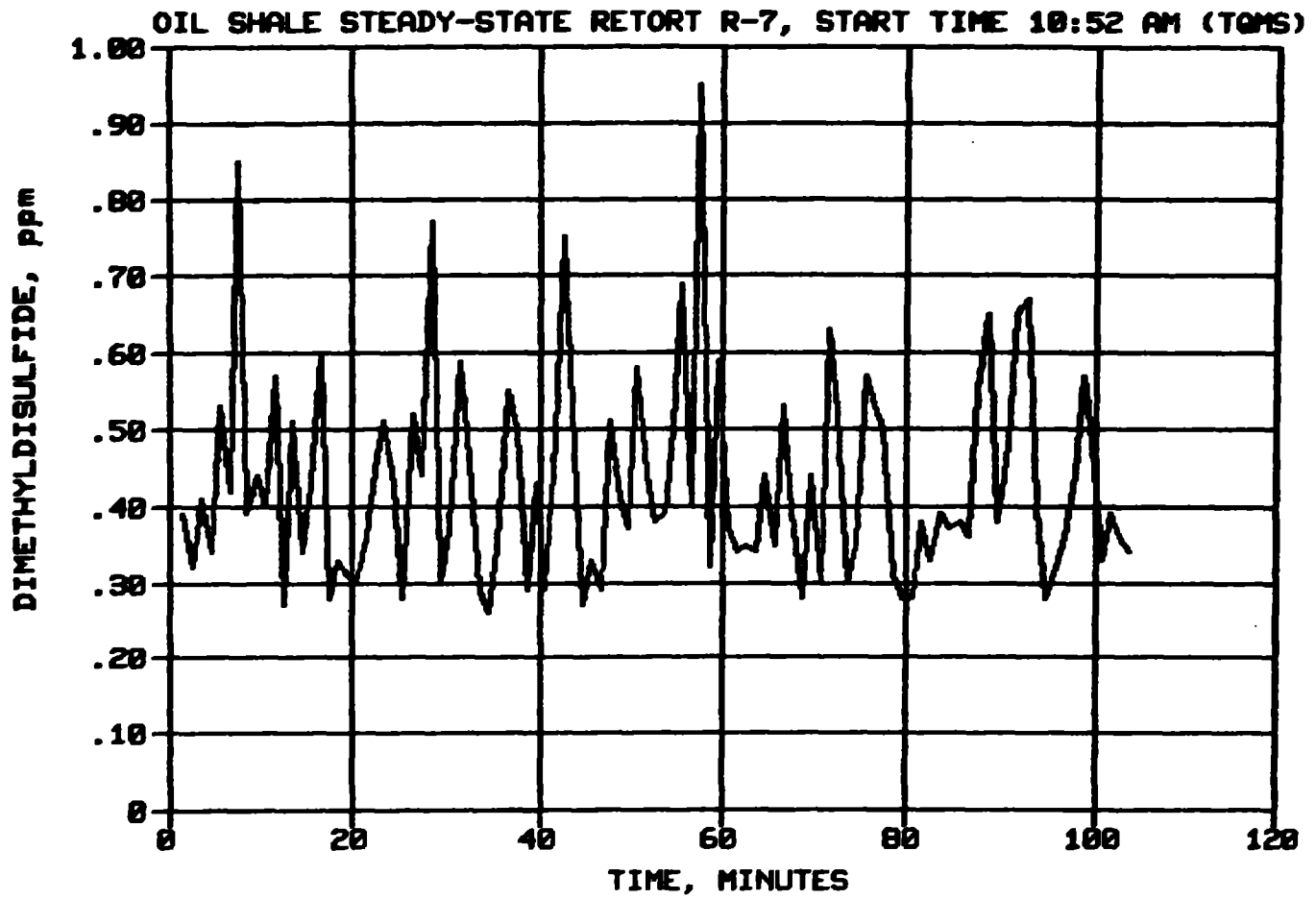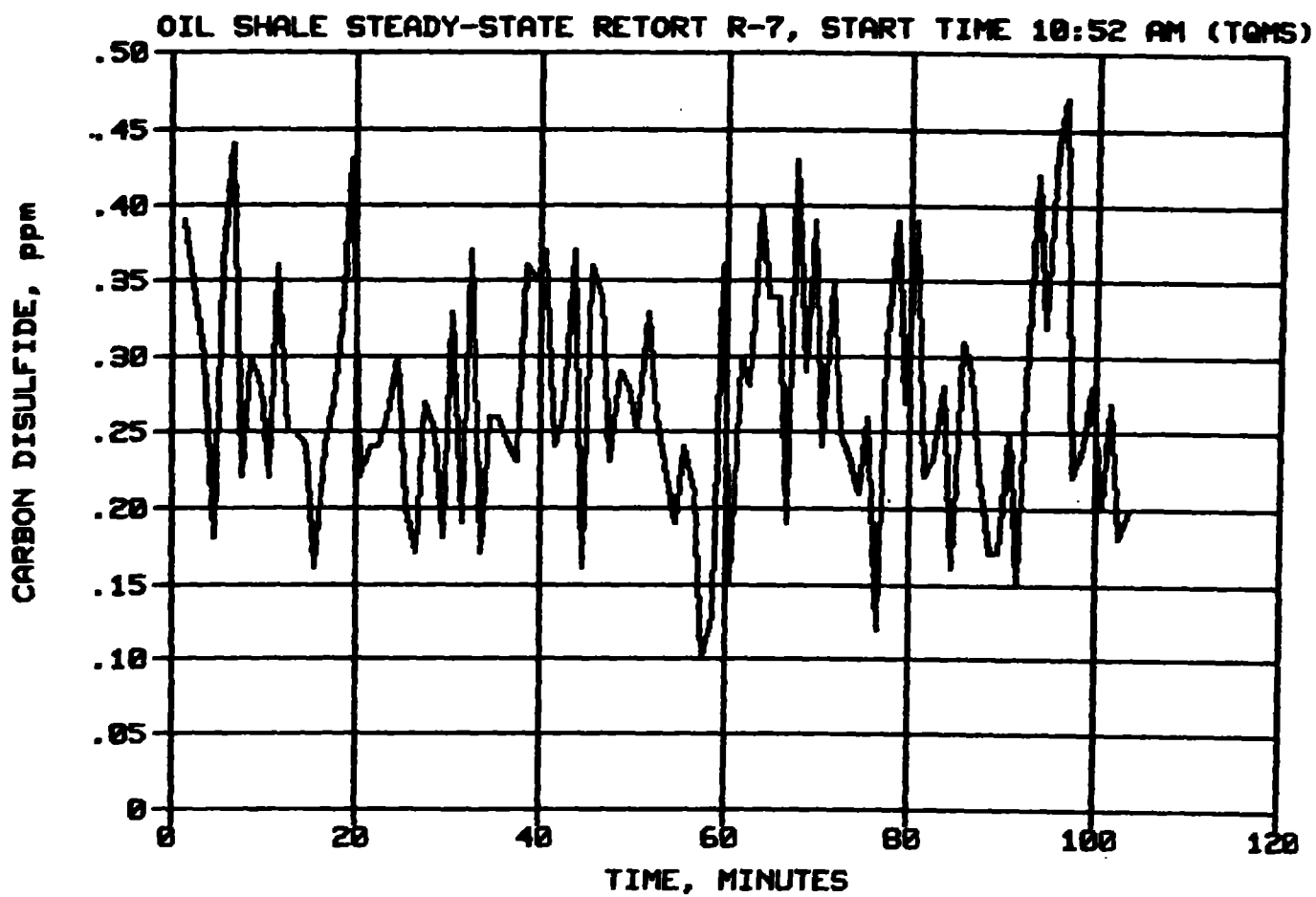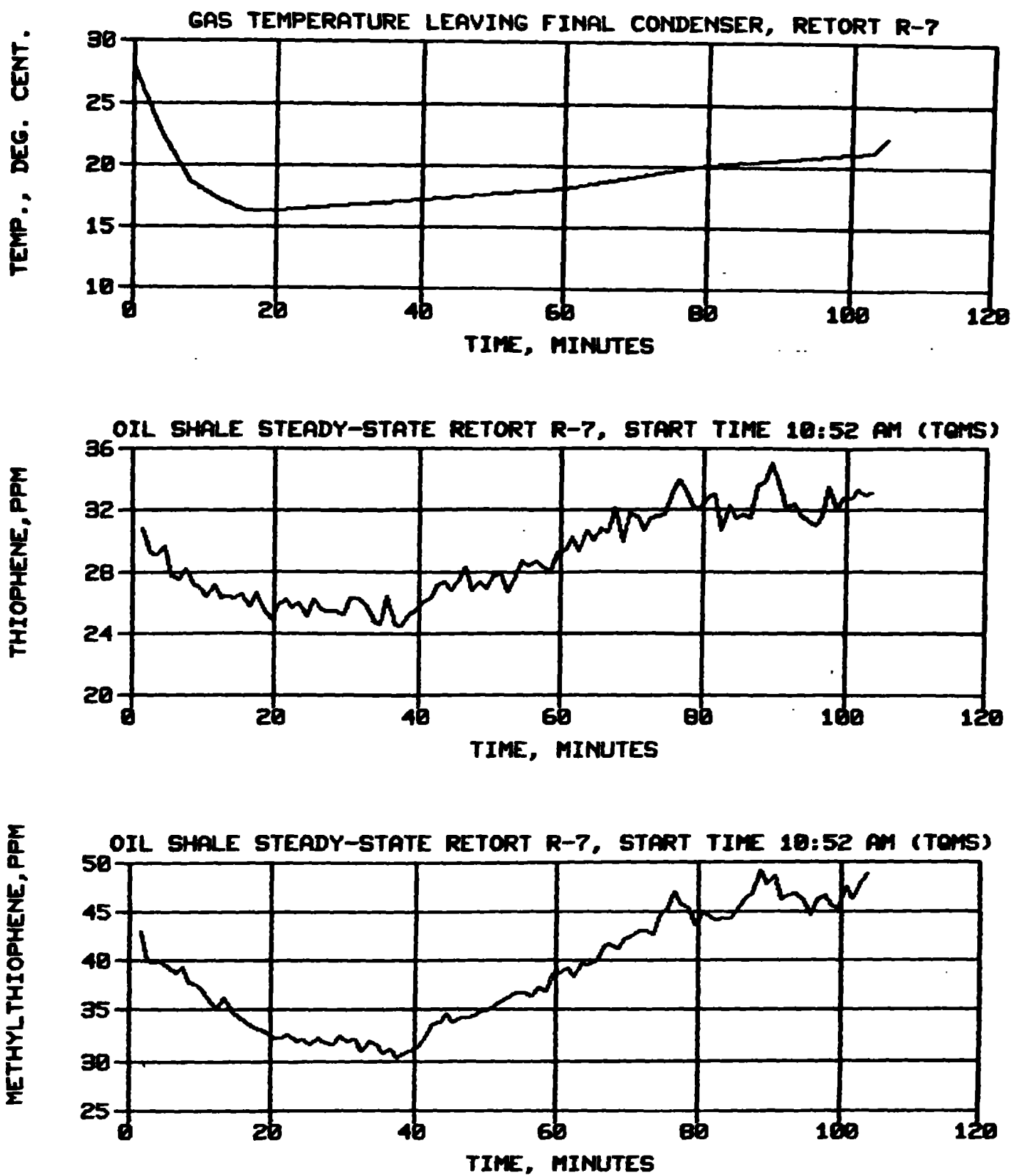
Appendix A

Experiments to Create Corrections for Grab Samples

When the bias in the H_2S results determined by the triple quadrupole
mass spectrometer (TQMS) for grab samples was discovered to be due to a sample
introduction problem, a series of experiments was carried out to determine the
cause and to see if corrections could be made to the existing data.
Fortunately, we were successful in both determining the cause and making the
corrections.

When we began our work introducing gas samples to the TQMS, we knew that
our inlet system was far from ideal. In particular, we knew that there were
potential problems with different leak rates through the needle valve based on
molecular weight and different responses of the ion gauge to the various
gases. Since we calibrated the instrument with sulfur gases mixed with
nitrogen introduced through the same inlet as samples, the molecular weight
problem was eliminated. We checked a reference book ("Vacuum Technology" by
Andrew Guthrie, Wiley & Sons, 1963) for ion gauge effects from different gases
and the included table suggested errors of plus and minus 20%. Based upon the
gross composition of the sample gas and these sensitivity factors, we
calculated that the sensitivity factors just about canceled.

One of the first experiments we carried out was a verification of the ion
gauge response to various pure gases that are the major constituents of the
oil shale pyrolysis gases. The inlet needle valve was set to give an ion
gauge reading in the TQMS source chamber of 6.00×10^{-6} torr with pure
nitrogen at one atmosphere. We then introduced one atmosphere of other pure
gases with the needle valve unchanged, and recorded the ion gauge reading.
Following are the results:

Gas	Ion Gauge Reading	Correction Factor
Nitrogen	6.00×10^{-6}	1.0
Hydrogen	3.95×10^{-6}	.66
Carbon Dioxide	10.15×10^{-6}	1.69
Carbon Monoxide	6.15×10^{-6}	1.03
Methane	11.2×10^{-6}	1.87
Toluene	See note	~ 6

Note: The toluene ratio was determined by a different method.

It can be seen that the factors taken from the reference are much smaller than measured. This can be due to a variety of factors which we will not dwell on. When we introduced the samples, the problem occurred when the needle valve was adjusted to give an ion gauge pressure of 6×10^{-6} torr.

We then checked the ion gauge response of several of the grab samples taken from R-6, with a range of gross gas composition. We found that there was an error factor of from 1.38 to 1.60 depending primarily on the sum of carbon dioxide and hydrocarbons in the sample. We also determined the ratio of the sulfur gases determined in these samples, introduced the old way and through the dual stage flow system. We found exactly the same error factor for the sulfur gases as seen in the pressure error, confirming that we had correctly identified the problem. Since the H_2S level in the grab samples had dropped to about 10 ppm due to adsorption or reaction, 150 ppm of H_2S was added to the bottle before determining the correction factor.

Since we had determinations of the gross composition of all gas samples as determined by the 103C analytical gas mass spectrometer, we were able to correct our previous results using the sum of the carbon dioxide and hydrocarbons in each sample. Since the dual-stage-pressure drop flow inlet is only borrowed from the Underground Coal Gasification project, we are designing a similar but less complex inlet for the TQMS to eliminate this problem in the future.

III. <u>VISITORS</u>

8/6-8/84   Larry Shadle and Catherine E. Gregorie from Morgantown Energy
           Technology Center in Morgantown, West Virginia.

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